

6

The Hydrogen Atom

Aims

By the end of this chapter you should be able to:

- Calculate the electron energy levels of the hydrogen atom from a knowledge of the Rydberg constant
- Understand the origins of the radial wave equation and the significance of the three energy terms that occur within it
- Explain the role of the three quantum numbers, n , l and m_l , in determining the overall structure and shape of the hydrogen atomic orbitals
- Demonstrate that the 1s wavefunction is indeed a solution of the Schrödinger equation for the hydrogen atom
- Understand the reasons why s-type wavefunctions have a maximum at the nucleus, whereas p- and d-type wavefunctions have a node there
- Calculate the distance from the nucleus at which a 1s electron is most likely to be found
- Understand the differences between the complex and real wavefunctions for p- and d-type wavefunctions

6.1 Introduction

In this chapter we shall consider atoms or ions which have a single electron. These include the hydrogen atom, He^+ and Li^{2+} . The solutions of Schrödinger's wave equation for such systems provide important information on the way in which an electron moves around the nucleus. The actual trajectory followed by an electron cannot be known in detail because of the operation of the uncertainty principle, but the wavefunctions obtained from the Schrödinger equation provide probability dis-

tributions for the position of the electron, and these are known as **atomic orbitals**. They can be contrasted with the accurately defined **atomic orbits** which would be required by classical physics.

The wavefunctions that we shall discuss form the basis of our understanding of atomic structure in general, because the concepts introduced can be extended to many-electron atoms. They will also prove useful when we come to discuss chemical bonding.

6.2 The Hydrogen Spectrum and the Quantization of Energy

The need for a quantum interpretation of the hydrogen atom arose from the spectrum of radiation emitted when an electric discharge was passed through hydrogen gas. In this process, electrons are promoted to higher energy states by the electric discharge, and photons are emitted when these electrons return to lower energy states. The energy released is given by the equation:

$$E_2 - E_1 = h\nu = \frac{hc}{\lambda} \quad (6.1)$$

where E_2 and E_1 are the energies of the upper and lower states, respectively. An electron moving in a classical orbit about the nucleus would be expected to emit radiation with a continuous range of wavelengths because there is no restriction on the energy that the orbiting electron can have. However, the actual spectrum consists of a series of lines with wavelengths that can be described by the formula:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (6.2)$$

In this equation, R is a constant, known as the **Rydberg constant**, and n_1 and n_2 are integers, with $n_2 > n_1$. Combining equations (6.1) and (6.2), we have:

$$E_2 - E_1 = hcR \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (6.3)$$

By associating E_2 with n_2 and E_1 with n_1 we can obtain the following equation for the allowed energies of the electron:

$$E_n = -\frac{hcR}{n^2} \quad (6.4)$$

where n must be an integer. The energies are negative because work has to be done to remove the electron from the region close to the nucleus

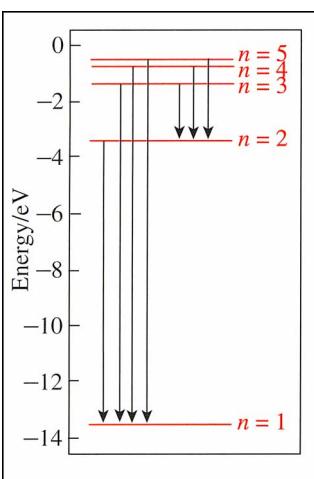


Figure 6.1 The energies of the allowed transitions in the spectrum of hydrogen

to infinity. The allowed energies and the transitions between them are illustrated in Figure 6.1.

Worked Problem 6.1

Q Calculate the energy of the state corresponding to $n = 1$ in units of electronvolts, using $R = 1.097 \times 10^7 \text{ m}^{-1}$.

A From equation (6.4):

$$E = -\left(6.626 \times 10^{-34} \text{ J s}\right) \times \left(2.998 \times 10^8 \text{ m s}^{-1}\right) \times \left(1.097 \times 10^7 \text{ m}^{-1}\right)$$

$$= 2.179 \times 10^{-18} \text{ J}$$

One electronvolt = $1.602 \times 10^{-19} \text{ J}$; hence:

$$E = -\frac{2.179 \times 10^{-18} \text{ J}}{1.602 \times 10^{-19} \text{ J} (\text{eV})^{-1}} = -13.60 \text{ eV}$$

This corresponds to the ionization energy of the hydrogen atom.

6.3 The Bohr Theory

In 1913, Bohr proposed a model for the hydrogen atom that appeared to explain the line spectra discussed in Section 6.2. The motion of the electron around the nucleus was considered to be similar to the motion of a planet around the sun, the gravitational attraction that keeps the planet in a circular or an elliptical orbit being replaced by the coulombic attraction between the electron and the positively charged nucleus. To account for the line spectra, Bohr postulated that the angular momentum of the electron was restricted to multiple values of \hbar . This was an arbitrary postulate at the time it was made, but it comes naturally from the quantum mechanical description of a particle moving in a circle, as we have already seen in Section 5.1.3.

Although the theory gives electron energies for the hydrogen atom which are in surprisingly good agreement with those calculated from equation (6.4), it fails to explain the energies and spectra obtained with other atoms, and it has now been completely superceded by quantum mechanics.

The Bohr theory has been mentioned here because the radius of the first Bohr orbit, known simply as the **Bohr radius**, is still widely used in quantum mechanics. It is given the symbol a_0 and has a value given by the formula:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 52.9 \text{ pm} \quad (6.5)$$

In this equation, ϵ_0 is the permittivity of free space, m_e is the mass of the electron and e is the electronic charge.

6.4 Formulation of the Schrödinger Wave Equation for Hydrogen-like Atoms

These atoms consist of an electron and a nucleus, both of which are in motion. Since wave-like properties have to be associated with both particles, the full wave equation for the atom involves a total of six variables, and such equations are usually difficult to solve. Fortunately, the motion of the atom as a whole can be separated into two parts: (a) the translational motion of the centre of mass, for which particle-in-a-box wavefunctions are appropriate, and (b) the motion of the nucleus and electron relative to the centre of mass (see Figure 6.2a).

It can be shown¹ that the second form of motion is mathematically equivalent to the movement of a hypothetical particle, with reduced mass μ , about a fixed point. The reduced mass is given by the formula:

$$\mu = \frac{m_e m_n}{m_e + m_n} \quad (6.6)$$

where m_e and m_n are the masses of the electron and nucleus, respectively.

This is illustrated in Figure 6.2b. For hydrogen, the mass of the nucleus is 1836 times that of the electron, and the reduced mass is therefore very close to the mass of the electron. It follows that little error is involved if the electron is considered to be moving about a stationary nucleus, and this approximation is even better with other, heavier nuclei.

The positive charge on the nucleus is equal to $-Ze$, where Z is the atomic number of the atom, and the electron is attracted towards this charge with a force given by the inverse square law:

$$\text{force} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad (6.7)$$

r being the distance of the electron from the nucleus. The potential energy, V , of the electron is defined as the work done in bringing the electron from infinity to some specified point close to the nucleus, and it is obtained from the integral:

$$V = \int_{\infty}^r \frac{Ze^2}{4\pi\epsilon_0 r^2} dr = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad (6.8)$$

Energy is actually released as the electron approaches the nucleus because the force is attractive, and V is therefore negative.

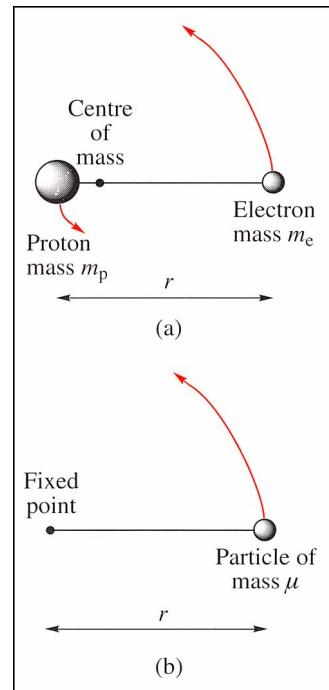


Figure 6.2 Diagram of the hydrogen atom: (a) the relative movements of the proton and electron about the centre of mass; (b) the mathematical equivalent of a particle of mass μ moving about a fixed point

The replacement of the relative motion of two particles with that of a hypothetical particle of mass μ , known as the **reduced mass**, is quite general, and has already been used in the description of the harmonic oscillator (Section 4.2.1) and the rotation of a diatomic molecule (Section 5.2.5).

In spherical polar coordinates the Schrödinger equation can now be written as:

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi \quad (6.9)$$

where:

$$\nabla^2 = \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \Lambda^2 \right] \quad (6.10)$$

and

$$\Lambda^2 = \frac{1}{\sin\theta} \left[\frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) \right] + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \quad (6.11)$$

6.5 The Radial Wave Equation

Solutions of the Schrödinger equation can be found which are the product of three functions, each one involving only one of the variables r , θ and ϕ . The wavefunction can therefore be written as:

$$\psi = R(r)\Theta(\theta)\Phi(\phi) \quad (6.12)$$

where the capital letters represent the functions and the lower case letters the associated variables. Substitution of this expression into equations (6.9) and (6.10) leads to:

$$-\frac{\hbar^2}{2\mu r^2} \left[\Theta\Phi \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + R\Lambda^2(\Theta\Phi) \right] - R\Theta\Phi \frac{Ze^2}{4\pi\epsilon_0 r} = ER\Theta\Phi \quad (6.13)$$

Here, the variables upon which the functions operate have been omitted to reduce the length of the equation. The functions $\Theta(\theta)$ and $\Phi(\phi)$ are found to be exactly the same as the wavefunctions which were discussed in Chapter 5 for a particle on the surface of a sphere. These are the spherical harmonics, $Y_{l,m_l}(\theta, \phi)$, which depend upon the two quantum numbers, l and m_l . Thus, $\Theta(\theta)\Phi(\phi) = Y_{l,m_l}(\theta, \phi)$. It was shown in Chapter 5 that the spherical harmonics are characterized by the equation:

$$\Lambda^2 Y_{l,m_l}(\theta, \phi) = -l(l+1) Y_{l,m_l}(\theta, \phi) \quad (6.14)$$

Combining this equation with equation (6.13) and writing Y in place of $\Theta(\theta)\Phi(\phi)$, we obtain:

$$-\frac{\hbar^2}{2\mu r^2} \left[Y \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - l(l+1) R Y \right] - \frac{Ze^2 R Y}{4\pi\epsilon_0 r} = E R Y \quad (6.15)$$

The spherical polar coordinates r , θ and ϕ were defined in Section 5.2.1. The same section also gives the Laplacian operator, ∇^2 , in terms of the variables r , θ and ϕ .

In equation (6.10) the partial differential $\partial/\partial r$ is used, indicating that the variables θ and ϕ are to be treated as constants during the differentiation. Because the functions Θ and Φ do not involve the variable r , we can write:

$$\frac{\partial}{\partial r} \left[r^2 \frac{\partial(R\Theta\Phi)}{\partial r} \right] = \Theta\Phi \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right)$$

Once Θ and Φ have been taken outside the bracket, the usual differential, d/dr , can be used. Similarly, $\Lambda^2(R\Theta\Phi) = R\Lambda^2(\Theta\Phi)$ because Λ^2 does not involve differentiation with respect to r .

The radial equation for the hydrogen atom is then obtained by dividing throughout by RY :

$$-\frac{\hbar^2}{2\mu r^2 R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} = E \quad (6.16)$$

This equation is very important because, without doing a lot of mathematics, it can provide a valuable insight into the motion of the electron about the nucleus. The first term in the equation involves the curvature of the radial component of the wavefunction, d^2R/dr^2 , and it represents the **radial kinetic energy** of the electron as it moves towards, or away from, the nucleus. The second term is identical to the right hand side of equation (5.32), and it therefore represents the **rotational kinetic energy** of the electron as it revolves around the nucleus. This term is also sometimes referred to as the **centrifugal energy**. The two forms of motion are illustrated in Figure 6.3. The third term is the **coulombic potential energy** arising from the electrical attraction between the electron and the nucleus. These three energy terms all vary with the distance of the electron from the nucleus, but their sum must be independent of r because it is equal to the total energy of the system, which is constant.

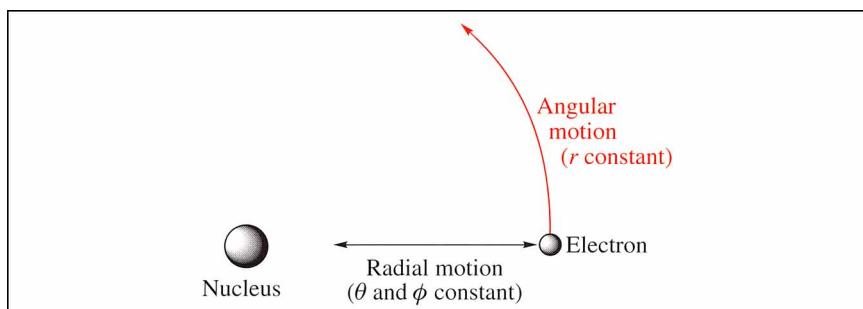


Figure 6.3 Illustration of the angular and radial motions of the electron

6.5.1 Solutions of the Radial Wave Equation

Equations similar to equation (6.16) have been studied by mathematicians, and acceptable solutions found. The mathematics involved are quite lengthy and will not be given here; they can be found in standard textbooks on quantum mechanics.² Two quantum numbers are needed to specify a particular radial wavefunction. The first one is the **azimuthal quantum number**, l , and the second one is a new quantum number n , often referred to as the **principal quantum number**. All the solutions have the same mathematical structure, which can be expressed by the equation:

$$R_{n,l}(r) = L_{n,l}(r) r^l e^{-Zr/na_0} \quad (6.17)$$

Strictly, the quantity referred to as a_0 in equation (6.17) should be the Bohr radius multiplied by m_e/μ . Since $m_e/\mu = 1.0005$ for the hydrogen atom, the error involved in making this approximation is negligible. We shall use this approximation frequently from now on.

Here, $L_{n,l}(r)$ is a polynomial in r , and a_0 is the Bohr radius, already mentioned in Section 6.3.

The quantum number n can take the values $n = 1, 2, 3, \dots$ and the quantum number l must always be less than n . Wavefunctions with $l = 0, 1$ and 2 are known as s, p and d orbitals, respectively. Thus, the wavefunction with $n = 2$ and $l = 1$ would be known as a 2p orbital.

The first few radial wavefunctions for hydrogen are listed in Table 6.1 and the way in which R and R^2 vary with distance from the nucleus is shown in Figure 6.4. The number of nodes (points where the wavefunction crosses the r axis) is equal to $n - l - 1$. The radial kinetic energy is related to the curvature of the wavefunction and increases with the number of nodes.

Table 6.1 The hydrogen-like radial wavefunctions $R(r)$ with $\sigma = Zr/a_0$, where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

Orbital type	n	l	$R_n(r)$ (not normalized)
1s	1	0	$e^{-\sigma}$
2s	2	0	$(2 - \sigma)e^{-\sigma/2}$
2p	2	1	$\sigma e^{-\sigma/2}$
3s	3	0	$(27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
3p	3	1	$(6 - \sigma)\sigma e^{-\sigma/3}$
3d	3	2	$\sigma^2 e^{-\sigma/3}$

Worked Problem 6.2

Q Use the radial wavefunctions for hydrogen, given in Table 6.1, to calculate the positions of the nodes for the 2s and 3s radial wavefunctions.

A The radial wavefunction, $R_{n,l}(r)$, goes to zero when the expression in front of the exponential term is equal to zero (see Table 6.1). For the 2s wavefunction, a node will occur when:

$$(2 - \sigma) = 0$$

where $\sigma = r/a_0$. Hence $r = 2a_0$.

For the 3s wavefunction we have to solve the quadratic equation:

$$27 - 18\sigma + 2\sigma^2 = 0$$

The roots of this equation are:

$$\sigma = \frac{18 \pm \sqrt{18^2 - (4 \times 2 \times 27)}}{4} = 1.90 \text{ and } 7.10$$

and nodes occur at $r = 1.90a_0$ and $7.10a_0$.

We see that the 3s wavefunction has its first node quite close to the node for the 2s wavefunction, but the second node is much further away from the nucleus.

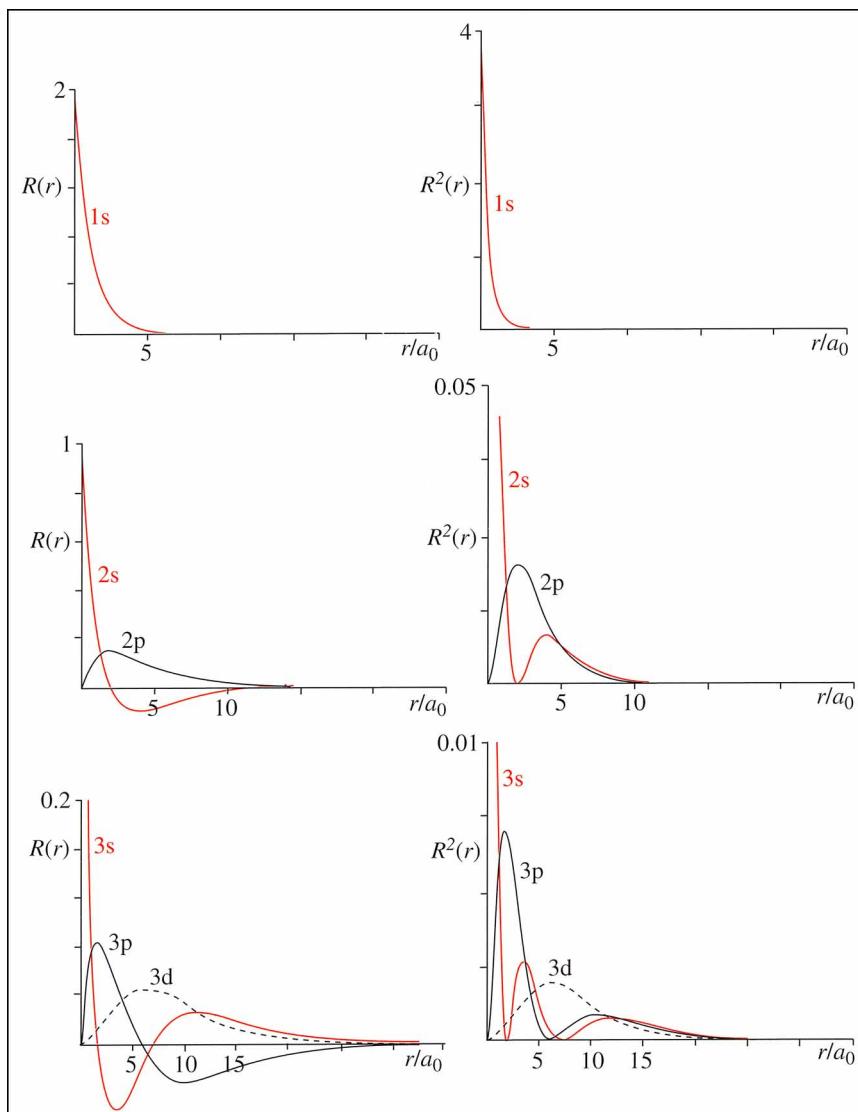


Figure 6.4 The variation of $R(r)$ and $R^2(r)$ with distance from the nucleus for the first few wavefunctions

6.5.2 A Relatively Simple Way to Find the Ground State Radial Wavefunction

One procedure for obtaining a solution of the radial wave equation is to make a guess as to the correct form of the wavefunction and see if it works. This is done in the example that follows.

Worked Problem 6.3

Q Show that the trial function $\psi = Ne^{-kr}$, where N and k are constants, is a solution of the Schrödinger equation for the hydrogen atom when the constant k has a particular value. Hence, calculate the energy associated with this wavefunction.

A Because the wavefunction does not depend upon the variables θ and ϕ , the spherical harmonic functions are not involved, and the operator Λ^2 can be omitted from equation (6.10). With $Z = 1$, the Schrödinger equation becomes:

$$-\frac{\hbar^2}{2\mu r^2} \left[\frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) \right] - \frac{e^2 \psi}{4\pi\epsilon_0 r} = E\psi \quad (6.18)$$

This equation can also be obtained from equation (6.16) by putting $\psi = R$ and noting that the quantum number $l = 0$.

Differentiation of the trial wavefunction gives:

$$\frac{d\psi}{dr} = -kNe^{-kr} = -k\psi$$

Therefore:

$$\frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \frac{d}{dr} \left(-kr^2 \psi \right) = \left(k^2 r^2 - 2kr \right) \psi.$$

Equation (6.18) then becomes:

$$-\frac{\hbar^2}{2\mu} \left[k^2 - \frac{2k}{r} \right] \psi - \frac{e^2 \psi}{4\pi\epsilon_0 r} = E\psi \quad (6.19)$$

Because E has to be constant, the terms in $1/r$ on the left-hand side must cancel one another out. This requires that:

$$\frac{\hbar^2 k}{\mu} = \frac{e^2}{4\pi\epsilon_0}$$

It follows that:

$$k = \frac{\mu e^2}{4\pi\epsilon_0\hbar^2} \quad (6.20)$$

A comparison with equation (6.5) shows that k is equal to the reciprocal of the Bohr radius a_0 , provided we ignore the small difference between m_e and μ .

Thus, a satisfactory solution of the wave equation is:

$$\psi = Ne^{-rla_0} \quad (6.21)$$

After the terms in $1/r$ have been removed from equation (6.19), we are left with:

$$E = -\frac{\hbar^2 k^2}{2\mu} = -\frac{\hbar^2}{2\mu} \left(\frac{\mu e^2}{4\pi\epsilon_0\hbar^2} \right)^2 = -\frac{\mu e^4}{32(\pi\epsilon_0\hbar)^2} \quad (6.22)$$

As we shall see in Section 6.6.1, this is the energy of the ground state, with $n = 1$.

6.5.3 Behaviour of the Radial Wavefunction Close to the Nucleus

It can be seen from Figure 6.4 that R has a maximum value at the nucleus when $l = 0$, but is zero at the nucleus when $l = 1$ and $l = 2$. To understand this difference, we need to examine what happens to the energy terms in equation (6.16) as the electron approaches the nucleus and r tends to zero. If $l = 0$, the second term in equation (6.16) is zero, showing that there is no rotational energy and all the motion is along a radius. It can be seen from Figure 6.5 that the coulombic potential energy tends towards $-\infty$ as the electron approaches the nucleus, and the radial kinetic energy must therefore tend towards $+\infty$, in order to keep the total energy constant. For this to happen, dR/dr must be negative as $r \rightarrow 0$, which means that R must have a maximum value at the nucleus.

When $l > 0$, the situation is significantly different because the centrifugal energy varies as $1/r^2$, and becomes the dominant term close to the nucleus. This energy acts like a repulsive force and counteracts the

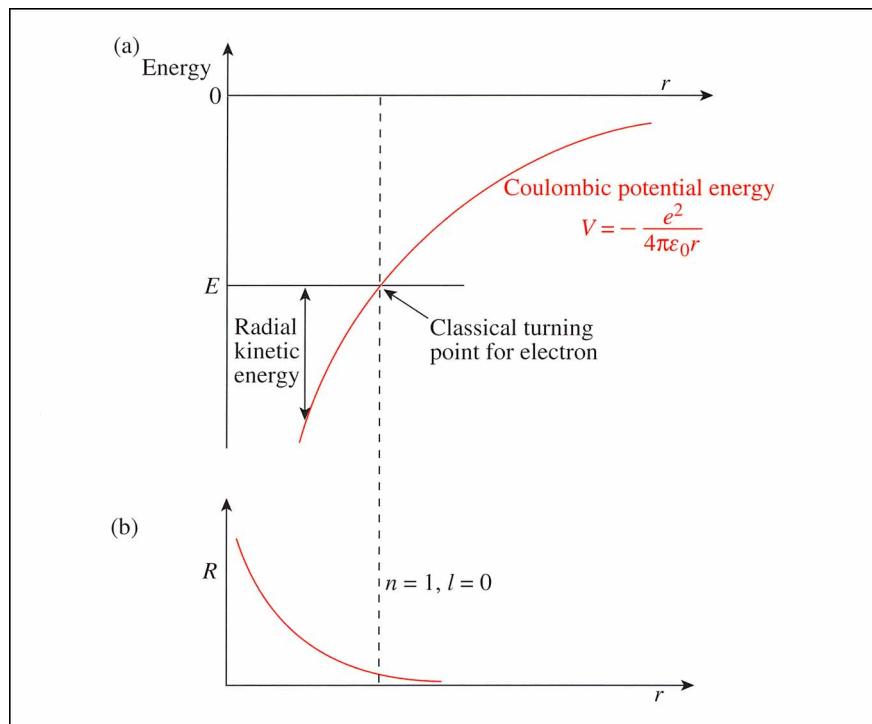


Figure 6.5 (a) The variation of the kinetic and coulombic potential energies of the electron with distance from the nucleus for $l = 0$, and (b) their effect on the radial wavefunction R . The dotted line represents the classical turning point for the electron; at greater distances the kinetic energy becomes negative and the electron can enter this region only by tunnelling

The radial kinetic energy of the electron also becomes negative at large distances from the nucleus where, owing to tunnelling, there is still a finite probability of finding it.

effect of the attractive coulomb potential. The variation of the centrifugal and potential energies with distance is shown in Figure 6.6, where it can be seen that the sum of the two energies becomes greater than the total energy, E , at distances less than a certain distance from the nucleus, r_c . This is a classically forbidden region, where the radial kinetic energy of the electron becomes negative. Although the electron can tunnel into this region (see Section 4.3.1), its wavefunction will decay away exponentially, and be zero at the nucleus.

6.6 The Full Hydrogen Atom Wavefunctions

The total wavefunction can be written as:

$$\psi = R_{n,l}(r)\Theta_{l,m_l}(\theta)e^{im_l\phi} \quad (6.23)$$

The forms taken by this wavefunction for various values of the quantum numbers n , l and m_l (up to $n = 2$) are shown in Figure 6.7. The function $e^{im_l\phi}$ is the same one that we had for a particle moving around a circle, and here it represents the motion of the electron in the xy plane. The allowed values of the quantum number m_l are as follows:

$$m_l = 0, \pm 1, \pm 2, \pm 3, \dots \text{ with } |m_l| \leq l$$

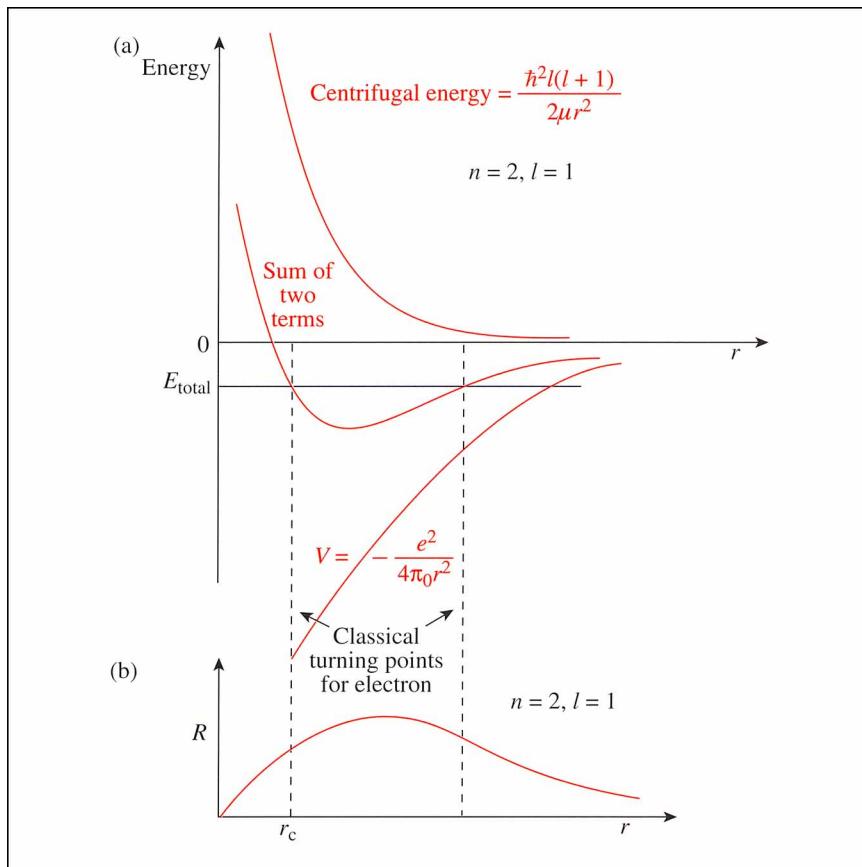


Figure 6.6 (a) The variation of the coulombic and centrifugal energies of the electron with distance from the nucleus for $l > 0$, and (b) their effect on the radial wavefunction R . There are two classical turning points and outside these limits the wavefunction decays away exponentially

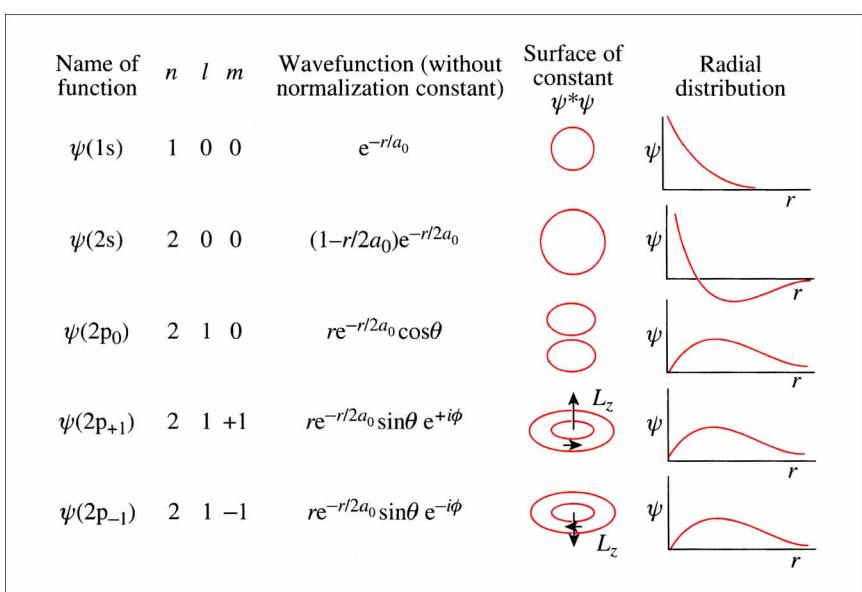


Figure 6.7 The mathematical form and shapes of the first five hydrogen orbitals

The form taken by the θ function depends upon the two quantum numbers, l and m_l .

When $l = 0$, m_l must also equal zero, and the θ function becomes a constant. Thus, there is no angular variation to the wavefunction, and we obtain an s orbital. When $l = 1$, m_l can have the values 0, ± 1 . For $m_l = 0$, $\Theta(\theta) = \cos\theta$ and we obtain a $2p_z$ orbital, but we do not get the familiar $2p_x$ and $2p_y$ orbitals when $m_l = \pm 1$. Instead, we obtain doughnut-shaped orbitals in which the electrons can be circulating in either a clockwise or an anti-clockwise direction, and the wavefunction now has a complex component.

6.6.1 The Energies

The energies are obtained by solving the Schrödinger equation (equation 6.9). It is found that only the principal quantum number n is involved in determining the energy, which is given by the equation:

$$E_n = \frac{-\mu Z^2 e^4}{32n^2 \pi^2 \epsilon_0^2 \hbar^2} \quad n = 1, 2, 3 \quad (6.24)$$

The mathematics involved in obtaining this equation are quite lengthy, and will not be discussed here. A relatively simple way of obtaining the energy when $n = 1$ and $Z = 1$ has already been given in Worked Problem 6.3.

6.6.2 Angular Momentum

The rotational motion of the electron around the nucleus is quantized in a similar way to that of a particle on the surface of a sphere, which was described in Chapter 5. The total angular momentum of the electron is equal to $\hbar[l(l+1)]^{1/2}$, and the component in the z direction is equal to $m_l\hbar$.

6.6.3 The s Orbitals

Motion of the s Electron and Shape of the Orbital

We have already seen that an electron has no rotational energy when $l = 0$ because the second term in equation (6.16) is zero. It follows that an s electron must undergo an oscillatory motion in a straight line through the nucleus, similar to that of a harmonic oscillator. Despite this similarity, the two forms of motion have different spatial properties because all directions in space are equivalent for an s electron, and the spherical shape of the s orbital arises from the uncertainty in the orientation of the oscillating electron. This is illustrated in Figure 6.8.

Although the circular orbit proposed by Bohr for an electron in the ground state of the hydrogen atom appeared to have some success, we now see that the actual motion of the electron is quite different. An oscillatory type of motion was originally considered by Bohr, but rejected as unacceptable because it would involve the electron colliding with the nucleus. This problem does not arise in such an acute form in wave mechanics because the positions of both nucleus and electron are uncertain, and neither can be precisely located without causing a major perturbation of the system.

Probability Distributions

The most probable place to find an s electron is at the nucleus because the wavefunction has a maximum value there. Thus, if we move an imaginary electron detector of fixed volume, dV , around the atom, we will get a maximum reading at the nucleus. The probability depends upon the volume of the detector, and is equal to $\psi^* \psi dV$. The term $\psi^* \psi$ is equal to the probability per unit volume, and is known as the probability density (see Section 1.4.2). For the 1s orbital:

$$\psi_{1s}^* \psi_{1s} = N^2 e^{-2r/a_0} \quad (6.25)$$

where N is a normalization constant. The variation of this expression with distance from the nucleus is shown in Figure 6.9a.

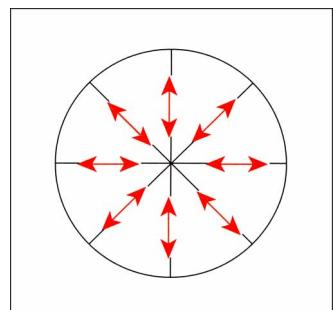


Figure 6.8 The movement of an electron in an s orbital

This is entirely a thought experiment because a real detector would perturb the electron to such an extent that no information about its original state could be obtained.

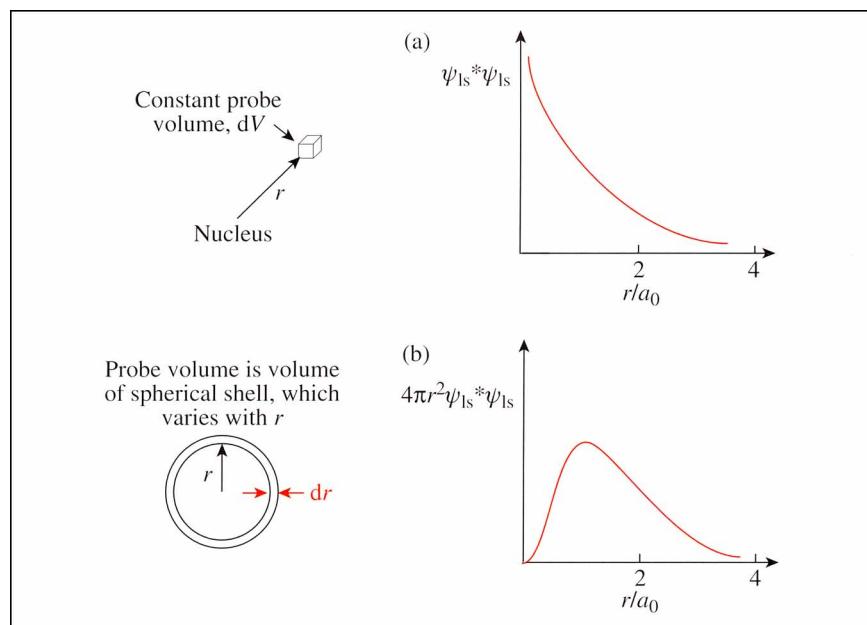


Figure 6.9 Two ways of recording the probability of an s electron being found at various distances from the nucleus: (a) using a constant volume probe; (b) using a spherical shell of variable volume

The volume of the spherical shell can be obtained by differentiating the equation for the volume of a sphere, $V = (4/3)\pi r^3$. Thus, $dV/dr = 4\pi r^2$.

A different type of probability distribution can be obtained by asking the question: “what is the probability of finding the electron at a distance between r and $r + dr$ from the nucleus?” In this case the volume element that we have to consider (see Figure 6.9b) gets bigger as we move away from the nucleus. The volume of the spherical shell, dV , is now equal to $4\pi r^2 dr$, and the probability of finding the electron between r and $r + dr$ is equal to $4\pi r^2 \psi^* \psi dr$.

Using the expression for $\psi_{1s}^* \psi_{1s}$ from equation (6.25), the probability per unit radial length, P_r , becomes:

$$P_r = 4\pi r^2 N^2 e^{-2r/a_0} \quad (6.26)$$

This function is plotted in Figure 6.9b, where it can be seen that the probability goes through a maximum value at a distance from the nucleus equal to the Bohr radius, a_0 . Close to the nucleus the r^2 term is dominant, which causes the probability to increase with r , but at distances greater than the Bohr radius the exponential term becomes dominant, and the probability falls with increasing r . It is surprising to find that the electron is most likely to be found at the Bohr radius, bearing in mind the large differences between the Bohr model and the wave mechanical one.

Worked Problem 6.4

Q Calculate the distance from the nucleus at which the 1s electron is most likely to be found.

A The maximum value of P_r can be obtained by putting dP_r/dr equal to zero. Hence:

$$\frac{dP_r}{dr} = 4\pi N^2 \left(2r - \frac{2r^2}{a_0} \right) e^{-2r/a_0} = 0$$

Ignoring the exponential term, which goes to zero as $r \rightarrow \infty$, there are two solutions: $r = 0$ and $r = a_0$. The first solution corresponds to a minimum and the second to a maximum. Thus, the electron is most likely to be found at $r = a_0$.

Differentiation of equation (6.26) with respect to the variable r is carried out using the product rule:

rule: $\frac{d(uv)}{dr} = u \frac{\partial v}{\partial r} + v \frac{\partial u}{\partial r}$, where u

and v are functions of r .

Normalization

The wavefunction for the 1s orbital can be written as:

$$\psi_{1s} = Ne^{-r/a_0} \quad (6.27)$$

where N is a normalization constant.

Worked Problem 6.5

Q Calculate the normalization constant for the hydrogen 1s orbital.

A We need to integrate P_r in equation (6.26) over all values of r , and equate the result to one. Thus:

$$\int_{r=0}^{r=\infty} 4\pi r^2 N^2 e^{-2r/a_0} dr = 4\pi N^2 \int_{r=0}^{r=\infty} r^2 e^{-2r/a_0} dr = 1$$

The integral is a standard form that can be looked up in mathematics textbooks:

$$\int_{x=0}^{x=\infty} x^n e^{-bx} dx = \frac{n!}{b^{n+1}}$$

Here, n is an integer and b is a constant. Replacing the variable x with r , and putting $n = 2$, $b = 2/a_0$, we find that the integral is equal to $(a_0^3)/4$. Thus:

$$4\pi N^2 \left(\frac{a_0^3}{4} \right) = 1$$

and:

$$N = \frac{1}{\sqrt{\pi a_0^3}} \quad (6.28)$$

6.6.4 The p Orbitals

We have already seen that the $2p_0$ orbital, shown in Figure 6.7, is the same as the familiar $2p_z$ orbital, but the $2p_{\pm 1}$ orbitals involve complex wavefunctions that are not so easy to visualize. For these orbitals, the electron is circulating around the nucleus in the xy plane, and has a component of angular momentum in the z direction equal to $\pm \hbar$.

The more familiar $2p_x$ and $2p_y$ orbitals take the forms:

$$\psi_{2p_x} = N_x x e^{-r/2a_0} \quad (6.29)$$

and

$$\psi_{2p_y} = N_y y e^{-r/2a_0} \quad (6.30)$$

where N_x and N_y are normalization constants, and x and y are Cartesian

Only wavefunctions with the same energy can be combined in this way to give another acceptable wavefunction. See Section 5.2.2.

coordinates. These functions can be obtained by a linear combination of the complex functions, as shown in the Appendix at the end of the chapter.

This procedure gives:

$$\psi_{2p_+} + \psi_{2p_-} = \sqrt{2}\psi_{2p_x} \quad (6.31)$$

and

$$\psi_{2p_+} - \psi_{2p_-} = \sqrt{2}\psi_{2p_y} \quad (6.32)$$

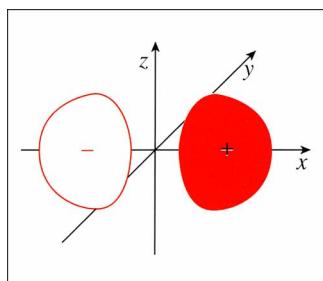


Figure 6.10 Surface of constant ψ for an electron in a $2p_x$ orbital

The shape of the $2p_x$ orbital can be deduced from equation (6.29). The presence of the Cartesian coordinate x in the expression for $2p_x$ means that there will be a node in the wavefunction in the yz plane. The surface of constant ψ is illustrated in Figure 6.10. The full three-dimensional orbital shape can be obtained by rotating the profile about the x axis. It is seen to consist of two doughnut-shaped lobes of opposite sign. The $2p_y$ orbital will be similar, but oriented along the y axis.

The $2p_x$ and $2p_y$ orbitals are not associated with any particular value of the angular momentum because they have been constructed from orbitals in which the electrons are moving in opposite directions. In this respect they are inferior to the $2p_{\pm 1}$ orbitals because some information has been lost, but their directional properties make them very important in chemical bonding.

6.6.5 The d Orbitals

These wavefunctions occur when $n \geq 3$ and $l = 2$. For each value of n there are five distinct orbitals, corresponding to $m_l = 2, 1, 0, -1, -2$. Each of the orbitals has a total angular momentum equal to $\sqrt{6}\hbar$, but they have different orientations, the component of angular momentum along the z axis being equal to $m_l\hbar$. The situation is similar to that shown in Figure 5.11 for the spherical harmonics.

Four of these wavefunctions are complex, because they include the term $e^{im_l\phi}$, but real wavefunctions can be obtained by combining pairs of complex wavefunctions with the same $|m_l|$, but opposite sign. The orbitals obtained by this process are listed in Table 6.2, and their shapes are shown in Figure 6.11. Linear combinations of the complex orbitals corresponding to $m_l = \pm 1$ give the $3d_{xz}$ and $3d_{yz}$ orbitals, whereas those with $m_l = \pm 2$ combine to give the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals. The $3d_{z^2}$ orbital, corresponding to $m_l = 0$, does not have a complex component.

Table 6.2 The real 3d wavefunctions

<i>n</i>	<i>l</i>	<i>m_l</i>	Real wavefunction (not normalized) ^a
3	2	0	$\psi(3d_{z^2}) = \sigma^2 e^{-\sigma/3} (3\cos^2 \theta - 1)$
3	2	±1	$\psi(3d_{xz}) = \sigma^2 e^{-\sigma/3} \sin \theta \cos \theta \cos \phi$ $\psi(3d_{yz}) = \sigma^2 e^{-\sigma/3} \sin \theta \cos \theta \sin \phi$
3	2	±2	$\psi(3d_{x^2-y^2}) = \sigma^2 e^{-\sigma/3} \sin^2 \theta \cos 2\phi$ $\psi(3d_{xy}) = \sigma^2 e^{-\sigma/3} \sin^2 \theta \sin 2\phi$

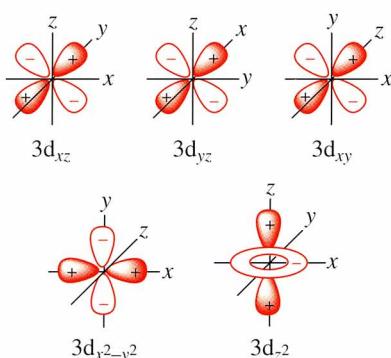
^a $\sigma = Zr/a_0$ 

Figure 6.11 Surfaces of constant $\psi^* \psi$ for the 3d orbitals. The sign of the wavefunction is indicated, but the probability density itself will, of course, always be positive. Note that the orientation of the Cartesian axes is not the same in all the figures

Appendix: Formation of the 2p_x and 2p_y Orbitals from the Complex 2p₊₁ and 2p₋₁ Orbitals

The 2p_x and 2p_y orbitals can be obtained by a linear combination of the complex functions:

$$\psi_{2p_{+1}} \pm \psi_{2p_{-1}} = N_{\pm 1} r e^{-r/2a_0} \sin \theta (e^{+i\phi} \pm e^{-i\phi}) \quad (\text{A6.1})$$

where $N_{\pm 1}$ is the normalization constant for the complex orbitals.

Now:

$$\begin{aligned} e^{+i\phi} \pm e^{-i\phi} &= [\cos \phi + i \sin \phi] \pm [\cos(-\phi) + i \sin(-\phi)] \\ &= [\cos \phi + i \sin \phi] \pm [\cos \phi - i \sin \phi] \\ &= 2 \cos \phi \quad \text{or} \quad 2i \sin \phi \end{aligned} \quad (\text{A6.2})$$

Hence:

$$\psi_{2p_+} + \psi_{2p_-} = 2N_{\pm l} r e^{-r/2a_0} \sin \theta \cos \phi \quad (\text{A6.3})$$

and

$$\psi_{2p_+} - \psi_{2p_-} = 2iN_{\pm l} r e^{-r/2a_0} \sin \theta \sin \phi \quad (\text{A6.4})$$

Referring back to Figure 5.7, it can be seen that $r \sin \theta \cos \phi$ is equal to the Cartesian coordinate x , and $r \sin \theta \sin \phi$ is equal to the coordinate y . The wavefunctions can therefore be written as:

$$\psi_{2p_+} + \psi_{2p_-} = 2N_{\pm l} x e^{-r/2a_0} \quad (\text{A6.5})$$

and

$$\psi_{2p_+} - \psi_{2p_-} = 2iN_{\pm l} y e^{-r/2a_0} \quad (\text{A6.6})$$

The function on the right-hand side of equation (A6.5) represents a $2p_x$ orbital because it has a node in the yz plane. Similarly, the function on the right-hand side of equation (A6.6) represents a $2p_y$ orbital. As they stand, these functions are not normalized. After normalization, which involves integration over all possible values of r , θ and ϕ , we can write:

$$\psi_{2p_+} + \psi_{2p_-} = \sqrt{2}\psi_{2p_x} \quad (\text{A6.7})$$

and

$$\psi_{2p_+} - \psi_{2p_-} = \sqrt{2}\psi_{2p_y} \quad (\text{A6.8})$$

Note that the “ i ” in equation (A6.6) has now disappeared.

Summary of Key Points

1. The wavefunction for the hydrogen atom can be expressed as the product of three functions in the variables r , θ and ϕ :

$$\psi = R_{n,l}(r)\Theta_{l,m_l}(\theta)e^{im_l\phi}$$

The mathematical form taken by the wavefunction is dependent upon three quantum numbers n , l and m_l . These quantum numbers can take integral values, subject to the following restrictions:

$$n = 1, 2, 3, \text{ etc.} \quad l < n \quad |m_l| \leq l$$

Orbitals with $l = 0, 1$ and 2 are known as s, p and d orbitals, respectively.

2. The motion of an electron in an s orbital is entirely along a radius, and the wavefunction has a maximum value at the nucleus. However, the electron is most likely to be found at a distance from the nucleus equal to the Bohr radius.
3. Electrons with $n = 2$, $l = 1$ and $m_l = 0, +1$ and -1 are said to occupy the $2p_0$, $2p_{+1}$ and $2p_{-1}$ orbitals, respectively. The $2p_0$ orbital is identical to the $2p_z$ orbital, but the other two orbitals are complex and differ from the more familiar $2p_x$ and $2p_y$ orbitals. The latter can be obtained by linear combinations of the two complex orbitals.
4. Electrons with $n = 3$, $l = 2$ and $m_l = 0, \pm 1, \pm 2$ are said to occupy the 3d orbitals. Four of these orbitals are complex, but real ones can be obtained by linear combinations of the complex orbitals.

Problems

6.1. Calculate the energy in eV required to excite an electron in a hydrogen atom from the $n = 1$ to the $n = 2$ state, given that the Rydberg constant is equal to $1.097 \times 10^7 \text{ m}^{-1}$.

6.2. Calculate the distance from the nucleus at which the 2s radial wavefunction has a minimum value.

6.3. Calculate the distance from the nucleus at which the radial wavefunction for the 3p orbital has (a) a node, (b) a maximum value and (c) a minimum value. Hence sketch the 3p radial wavefunction.

6.4. At what distance from the nucleus is an electron in a hydrogen 2s orbital most likely to be found? *Hint:* there are two maxima in

the radial probability curve, separated by a node at $r = 2a_0$. The second maximum is larger than the first and is therefore the one that is required.

6.5. For the 1s orbital of the hydrogen atom, calculate the average distance, $\langle r \rangle$, of the electron from the nucleus. *Hint:* $\langle r \rangle = \int_0^\infty r P(r) dr$, where $P(r)$ is the probability per unit length (see equation 6.26).

You will also need to use the standard integral: $\int_0^\infty x^n e^{-bx} dx = \frac{n!}{b^{n+1}}$, where n is an integer and b is an arbitrary constant.

6.6. Show that the radial wavefunction

$$R(r) = N r e^{-r/2a_0}$$

where N is a normalization constant, is a solution of equation (6.16) when the quantum number $l = 1$. Hence, calculate the energy of this state.

6.7. At what distance along the z axis is an electron in a $2p_z$ orbital of a hydrogen atom most likely to be found? *Note:* this is not the same as the most probable radius. The correct answer will be obtained by considering a probe of constant volume, which is moved along the z axis.

6.8. In one of the excited states of the hydrogen atom, the electron has a total orbital angular momentum of $\sqrt{2}\hbar$ but no component of angular momentum along the z axis. The minimum energy required to remove the electron from the atom is 3.4 eV. Which orbital does the electron occupy?

6.9. The d orbitals, corresponding to the quantum numbers $n = 3$, $l = 2$ and $m_l = \pm 1$, have the following wavefunctions:

$$\psi = R(r) \sin \theta \cos \theta e^{\pm i\phi}$$

where $R(r)$ is the radial wavefunction. What real wavefunctions can be obtained from these complex wavefunctions?

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1. P. W. Atkins, *Physical Chemistry*, 6th edn., Oxford University Press, Oxford, 1998, p. 346.
2. R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles*, 2nd edn., Wiley, New York, 1985, appendix N.

Further Reading

- D. A. McQuarrie and J. D. Simon, *Physical Chemistry: A Molecular Approach*, University Science Books, Sausalito, California, 1997, chap. 6.
- P. W. Atkins and R. S. Friedman, *Molecular Quantum Mechanics*, 3rd edn., Oxford University Press, Oxford, 1997, chap. 7.